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The Chemistry and Isotopic Composition of Waters in the Low-Enthalpy Geothermal System of Cimino-Vico Volcanic District, Italy

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ABSTRACT

Geothermal energy exploration is based in part on interpretation of the chemistry, temperature, and discharge rate of thermal springs. Here we present the major element chemistry and the δD, $\delta^{18}O$, $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ of groundwater from the low-enthalpy geothermal system near the city of Viterbo in the Cimino-Vico volcanic district of west-Central Italy. The geothermal system hosts many thermal springs and gas vents, but the resource is still unexploited. Water chemistry is controlled by mixing between low salinity and HCO_3-rich fresh waters (<24.2°C) flowing in shallow volcanic rocks and SO_4-rich thermal waters (25.3°C to 62.2°C) ascending from deep, high permeability Mesozoic limestones. The (equivalent) SO_4/Cl (0.01-0.02), Na/Cl (2.82-5.83) and B/Cl (0.02-0.38) of thermal waters differs from the ratios in other geothermal systems in Central Italy, probably implying a lack of hydraulic continuity across the region. The $\delta^{18}O$ (-6.6‰ to -5.9‰) and δD (-40.60‰ to -36.30 ‰) of spring water suggest that the recharge area for the geothermal system is the summit region of Mount Cimino. The strontium isotope ratios ($^{87}Sr/^{86}Sr$) of thermal waters (0.70797-0.70805) are consistent with dissolution of the Mesozoic evaporite-carbonate units that make up the reservoir, and the ratios of cold fresh waters mainly reflect shallow circulation through the volcanic cover but some admixture (<10%) of thermal water as well. The boron isotope composition ($\delta^{11}B$) of fresh waters (-5.00 and 6.12‰) is similar to those of the volcanic cover, but the $\delta^{11}B$ of thermal waters (-8.37‰ to -4.12‰) is a mismatch for the Mesozoic reservoir rocks and instead reflects dissolution of secondary boron minerals during fluid ascent through flysch units that overlie the reservoir. A slow and tortuous ascent enhances extraction of boron but also promotes conductive cooling, partially masking the heat present in the reservoir. Overall data from this study is consistent with previous studies that concluded that the geothermal system has a large energy potential.

1. Introduction

In the past few decades the development of geothermal energy resources has expanded worldwide as a sustainable and renewable source for electricity generation and heating applications (e.g. Moore and Simmons, 2013). Geothermal systems are classified based on the reservoir temperature and there are various criteria for their classification (Williams et al., 2011). Low-enthalpy (or low-temperature) geothermal systems have been classified by the U.S. Geological Survey as those with reservoir temperatures of less than 90 °C (Reed, 1983; Williams et al., 2008) and by others at <125 °C (Hochstein, 1988), and <150 °C (e.g. Nicholson, 1993). In many countries low-enthalpy geothermal resources are typically used for bathing, heating, greenhouses, and ground source heat pumps (Lund et al., 2011; Moore and Simmons, 2013); they can also be exploited for electric power generation if sufficiently low temperatures are available for cooling the working fluid in a binary power plant (Williams et al., 2008).

Geothermal energy exploration is based in large part on the characterization of water, gas, and rock chemistry, reservoir permeability, and the rates of water recharge into the reservoir. In the past several decades many geochemical indicators have been developed to assess the state of the geothermal reservoir to reduce the high costs of exploratory drilling (e.g. Arnórsson, 2000; Boschetti, 2013; Capaccioni et al., 2014; Fournier, 1981; Fournier and Truesdell, 1973; Fournier, 1977; Giggenbach, 1988, 1992; Spycher et al., 2011). In geothermal resource exploration and assessment**,** the stable isotopes of water ($\delta^{18}O$ and δD) have been widely used as tracers for the origin of groundwater and for water-rock interaction, and as indicators for mixing of waters from different sources. The isotopic composition of strontium ($^{87}Sr/^{86}Sr$) provide**s** information on flow paths and mixing of waters because strontium is readily leached from rocks (e.g. Boschetti et al., 2005; Dotsika et al., 2010; Lee et al., 2011; ; Negrel et al., 1999; Peiffer et al., 2011; Pennisi et al., 2006). Boron stable isotopes are applied in geothermal exploration, because boron is highly incompatible during the water-rock interaction and because incorporation of boron into secondary

61 minerals fractionates its isotopes (e.g. Ellis and Mahon, 1964, 1967; Leeman et al., 2005; Millot et
62 al., 2012; Palmer and Sturchio, 1990).

63 In this study we present the major element chemistry and the δD, $\delta^{18}O$, $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ of
64 groundwater from the low-enthalpy geothermal system near the city of Viterbo in the Cimino-Vico
65 volcanic district of west-Central Italy (Figure 1). The region hosts many thermal springs and gas
66 vents and is a part of a larger thermally anomaly that extends from southern Tuscany in the north to
67 the active volcanic areas of Phlegrean Fields and Vesuvius (Figure 1). The geothermal resource in
68 the area is still unexploited despite its large potential (Cinti et al., 2014, 2015). The specific goals of
69 this study are to (1) characterize the processes controlling water chemistry in the Cimino-Vico area,
70 (2) characterize the processes controlling the isotopic systematics of boron and strontium in low
71 enthalpy hydrothermal systems, and (3) use the geochemical and isotopic data to provide new
72 insights on the groundwater circulation in the area, which in turn, provide information on the
73 potential for geothermal energy production.

74 **2. Geological framework**

75 Volcanic activity which gave rise to the Cimino and Vico complexes started at 1.35 Ma with
76 explosive and effusive activity of the Cimino complex. Between 0.8 and 0.3 Ma, the Vico complex
77 was active, with a central caldera that now hosts Vico Lake (Figure 1). The Cimino volcanic
78 products include rhyodacites, latitic ignimbrites and olivine-latitic lavas, and are mostly covered by
79 the K-alkaline pyroclastic deposits from the Vico volcanics, consisting of undersaturated trachytes,
80 phonolites, tephritic phonolites, tephrites, and subordinate tuffs (Arnone, 1979; Gambardella et al.,
81 2005; Sollevanti, 1983). Northwest and northeast striking extensional faults divide the substratum
82 rocks and control the horst and graben pattern (Baiocchi et al., 2013). Ongoing magmatic activity is
83 manifested by several geothermal anomalies, thermal springs, CO_2-rich vents and active travertine
84 deposition.

85 The hydrogeology of the Cimino-Vico geothermal area has been widely studied and the

hydrostratigraphic sequence was defined (Angelone et al., 2008; Arnone, 1979; Baiocchi et al., 2013; Chiocchini et al., 2010; Piscopo et al., 2006) (Figure 2). The high permeability Mesozoic limestone in Central Italy is the primary regional groundwater aquifer which hosts numerous geothermal reservoirs with temperatures ranging between 48°C and 115°C (Minissale, 2004). The reservoir temperature of Cimino-Vico geothermal system is ~94°C, based on multicomponent geothermometry (Battistel et al., 2014). Abundant CO_2 from active metamorphism is dissolved in the aquifer (Chiodini et al., 1999; Duchi et al., 1987; Minissale and Duchi, 1988). The shallow (<200 m) fresh-water aquifer in the volcanic products of Cimino and Vico and the deep regional aquifer are separated by low-permeability Pliocene-Pleistocene sediments and Cretaceous-Oligocene flysch deposits (Ligurian Units) (Figure 2). Thermal groundwater from the deep reservoir ascends through fractures and faults in the sedimentary substratum (Angelone et al., 2008; Arnone, 1979; Baiocchi et al., 2012; Chiocchini et al., 2010; Piscopo et al., 2006). The aquifer system is bounded laterally by the Pliocene- Pleistocene sedimentary complex and Cretaceous-Oligocene flysch units.

3. Sampling and laboratory analysis

Twenty-three water samples from springs and private wells (Figure 1) used for agricultural water supply were sampled between October 2011 and August 2012. Samples for major element chemistry were collected in 50 ml high-density polyethylene bottles and filtered in the field with a 0.45 μm filter. Water temperature, electrical conductivity (EC) and pH were measured in the field. Alkalinity was determined in the field by titration with 0.1 N HCl. Major element concentrations were determined at the Geochemistry laboratory of Sapienza University in Rome with a Dionex DX-120 ion chromatograph (precision ±2%) with a Dionex CS-12 column for cations and a Dionex AS9-SC column for anions. Nine samples were collected in 50 ml cleaned glass bottles and analysed for $\delta^{18}O$ and δD compositions at the U.S. Geological Survey Stable Isotope Laboratory in Reston, Virginia. $\delta^{18}O$ values were determined using the CO_2 equilibration technique of Epstein and

111 Mayeda (1953), which has been automated (Révész and Coplen, 2008). δD compositions were
112 determined using a hydrogen equilibration technique (Coplen et al., 1991; Révész and Coplen,
113 2008). The 2σ uncertainties of oxygen and hydrogen isotopic results are 0.2‰ and 2‰, respectively
114 and the results are reported in per mill (‰) relative to VSMOW (Vienna Standard Mean Ocean
115 Water).

116 Fourteen additional filtered samples were collected in 15 ml high-density polyethylene bottles
117 for strontium and boron concentrations and isotope analyses. The samples were acidified with ultra-
118 pure nitric acid to a pH of about 2 in the field. Strontium and boron concentrations were measured
119 at the Geochemistry laboratory of Sapienza University in Rome using ICP-MS (X Serie 2 Thermo
120 Fisher Scientific) with an analytical accuracy of 2% to 5%. The strontium isotope ratios were
121 measured on a Finnigan MAT 261 Thermal Ionization Mass Spectrometer (TIMS) at the USGS
122 Metal and Metalloid Isotope Laboratory in Menlo Park, CA. Reported values have been corrected
123 for natural and analytical stable isotope fractionation to $^{88}Sr/^{86}Sr = 8.37515$ and then adjusted to the
124 NBS987 standard value of 0.71024. The values are precise to 0.00002 at the 95% confidence level.
125 Boron isotope analysis were carried out by negative TIMS (Vengosh et al., 1989; Zeininger and
126 Heumann, 1983) at the USGS Metal and Metalloid Isotope Laboratory in Menlo Park, CA.
127 Sufficient water to supply 2 ng of B was loaded directly onto degassed, zone-refined Re filaments.
128 The B isotopes were measured as the BO_2 species at masses 42 and 43. The typical agreement of
129 replicate analyses of a sample is within 1‰. Isotope ratios are reported as permil deviation ($\delta^{11}B$) in
130 the $^{11}B/^{10}B$ ratios relative to the standard NBS SRM 951 and the analytical precision is ±0.5‰ as
131 $\delta^{11}B$.

132 **4. Results**

133 The chemical composition of groundwater samples from Cimino-Vico thermal area is reported
134 in Table 1. The charge balance of all samples is within ±4%. The waters sampled are classified as
135 either HCO_3-rich fresh waters (T< 25°C, 6.4<pH< 7.4, HCO_3/SO_4 of 1.1-16.4 equivalent) or SO_4-

136 rich thermal waters (T>25°C, 5.8>pH> 7.0, HCO_3/SO_4 of 0.3-1.7 equivalent) (Figures 3-6, Table 1).
137 The thermal waters have Cl/SO_4 and Na/Cl equivalent ratios ranging from 0.01 to 0.02 and 2.52 to
138 5.83 respectively, which considerably differ from the values of other thermal waters in Central Italy
139 (e.g. Minissale et al., 2002). The B/Cl equivalent ratio ranges from 0.003 to 0.04 in the fresh waters
140 and from 0.02 to 0.38 in the thermal samples.

141 The cation composition of thermal waters ranges between the composition in geothermal well
142 Vetralla 001 VET1 drilled to a depth of 1117 m within the Mesozoic units ~20 km south of the
143 study area (http://unmig.sviluppoeconomico.gov.it/unmig/geotermia/pozzi/dettaglio.asp?cod=136)
144 and the NaK-rich composition of the Vico rocks (Figure 4). Few thermal water samples bear the
145 signature of the Na^+- and K^+-rich volcanic substrate of the Cimino-Vico area (Arnone, 1979;
146 Gambardella et al., 2005; Sollevanti, 1983). The high concentration of Ca^{2+} (<881 mg/L) and SO_4
147 (<1,826 mg/L) in thermal waters traces the interaction with gypsum constituting the Mesozoic units.
148 There is only a weak correlation between water temperature and dissolved ions concentrations,
149 suggesting rapid cooling of the ascending waters.

150 *Isotopic composition of waters*

151 The $\delta^{18}O$ and δD values of all samples range between -6.6‰ to -5.9‰ and from -40.60‰ to -
152 36.30 ‰, respectively (Table 1, Figure 7) and strontium isotope ratios ($^{87}Sr/^{86}Sr$) range between
153 0.70797 and 0.71026 (Table 1, Figure 8). The $^{87}Sr/^{86}Sr$ values of thermal waters have a narrow
154 range (0.70797-0.70805) and are similar to those of the Mesozoic evaporite-carbonate units
155 (0.70778±0.000110; Boschetti et al. 2005). The cold fresh waters have a wider range of values
156 (0.71086-0.70852) which are generally higher than the ratios in thermal waters, and extend to the
157 values of the volcanic rocks from the Cimino-Vico district, 0.7107-0.7136 (Hurley et al., 1966; Poli
158 et al., 1984; Vollmer, 1976). $\delta^{11}B$ in thermal waters ranges from -8.37‰ to -4.12‰, and in fresh
159 waters between -5.00 and 6.12‰ (Table 1, Figures 9,10). Samples #14 and #15 have positive $\delta^{11}B$
160 values of 3.25 and 6.12‰, respectively.

5. Discussion

The chemical and isotopic data we have acquired provide new insights on the low-enthalpy Cimino-Vico hydrothermal system. We first discuss the processes that control the groundwater chemistry and then the systematics of strontium and boron isotopes. The data help us resolve groundwater flowpaths, mixing relations, and ultimately energy resource available. The approach we use may be applicable to other, similar low-enthalpy systems in central Italy and elsewhere.

5.1 Processes controlling water chemistry

The relatively high temperature of groundwater ascending from depth, the high rate of CO_2 degassing, and the mixing between thermal and fresh waters are reflected in the chemical composition of spring waters in the Cimino-Vico District (Figures 3 and 4). The chemical composition of the thermal waters suggests that in the geothermal reservoir, fluids are in equilibrium with gypsum, quartz, aragonite and calcite (Battistel et al., 2014). The dissolution of sulphate minerals results from groundwater flow in the Mesozoic evaporite-carbonate sequence as inferred from the positive correlation between $Ca^{2+}+Mg^{2+}$ and SO_4^{2-}. The enrichment in $Ca^{2+}+Mg^{2+}$ compared with $Na^{+}+K^{+}$ (Figures 4, 5) suggests insignificant contributions from silicate weathering in thermal waters.

High HCO_3^- concentrations in fresh waters reflect the dissolution of carbonates and CO_2 degassing from the deep geothermal reservoir through the local fault system. The $(Ca^{2+}+Mg^{2+})/ HCO_3^- \approx 1$ also implies that carbonate dissolution is significant (Figure 5). Silicate weathering is evident in the chemistry of fresh water samples. The dissolution of Na-K-bearing silicate minerals such as leucite and plagioclase, likely resulting from the ingress of CO_2 in the volcanic aquifer increases the ratio $Na^{+}+K^{+}/ Ca^{2+}+Mg^{2+}$. Similar to other low-enthalpy geothermal systems, the chemistry of low enthalpy thermal waters of Cimino-Vico system is mainly lithology-dependent and controlled by rock dissolution. In contrast, the chemical composition of high enthalpy thermal fluids is mainly controlled by temperature-dependent reactions between primary and secondary, alteration

minerals and by cation exchange processes that result in ion ratios much different from those in the host rock (Figure 6).

The uniform $\delta^{18}O$ and δD values of Cimino-Vico volcanic waters that plot along the Meteoric Water Line (Figure 7) suggest a meteoric origin for thermal waters. The $\delta^{18}O$ and δD show a progressive isotope lightening from the Tyrrhenian Sea to the Apennines Chain. The proposed vertical isotope gradient for Central Italy (-0.3‰ per 100 m; Cinti et al., 2014; Longinelli and Selmo, 2003; Minissale and Vaselli, 2011; Zuppi et al., 1974,) suggests that recharge is at an elevation of 400 m to 700 m on the summit of Mount Cimino, consistent with previous studies (Baiocchi et al., 2006; Cinti et al., 2014; Piscopo et al., 2006). A slight negative shift in $\delta^{18}O$ values of thermal waters likely results from oxygen exchange between water and CO_2 derived from geothermal activity (Negrel et al., 1999):

$$0.5\ C^{16}O_2 + H_2{}^{18}O = 0.5\ C^{18}O_2 + H_2{}^{16}O. \quad (1)$$

The relatively low temperature in the geothermal reservoir (Battistel et al., 2014) and the relatively large effect of the CO_2 on the $\delta^{18}O$ value imply that fluid-rock interaction has a minimal effect on the isotope ratio (Figure 7).

5.2 Processes controlling B and Sr systematics

The $^{87}Sr/^{86}Sr$ values in the thermal waters show that the major source of strontium is the Mesozoic formations hosting evaporite deposits (Figure 8). Overall, the $^{87}Sr/^{86}Sr$ values show that both thermal and fresh waters are actually variable mixtures of the two end-member fluids. The isotopic ratio of fresh waters samples implies that the fraction of water that circulates only through the Vico volcanic rocks is 0.9-1 (Figure 8); up to 10% of the water is from the thermal reservoir. The presence of faults cutting the intervening low-permeability units facilitates the ascent of the thermal fluids to the surface and the connection between the two aquifers.

In hydrothermal systems, both boron and chloride are readily leached from rocks (Ellis and Mahon 1964, 1967), although high Cl content can also be derived from magma degassing of HCl. Boron concentrations in water higher than 1 mg/L are generally attributable to hydrothermal influence (Hem, 1985), and the Cimino-Vico thermal waters mostly meet this criterion. However the Cimino-Vico hydrothermal system shows a lower chloride content compared to other geothermal systems (e.g. Central Italy: Boschetti et al., 2005; Minissale et al., 1997; Minissale et al., 2002; Pennisi et al., 2006. Rest of the world: Arnórsson and Andrésdóttir, 1995; Dotsika et al., 2010; Millot and Négrel, 2007; Palmer and Sturchio, 1990). Such low Cl concentrations suggest a highly permeable reservoir that has been flushed repeatedly with water and a reservoir that is isolated from inputs of magmatic brine or sources of chloride from adjacent geothermal systems. So the question arises as to why so much boron is still being leached from the subsurface.

We propose that boron, like chloride, has already been removed from the Mesozoic reservoir rocks and the elevated B content in the thermal waters is attributable to the dissolution of the borosilicate minerals making up the Ligurid units. Flysch rocks are naturally rich in boron (Pennisi et al., 2000) and in this setting could have been further enriched if the boron removed from the underlying Mesozoic rocks was redeposited into secondary formation minerals like tourmaline, during perhaps a previous stage of high enthalpy hydrothermal activity.The aggressiveness of the presently ascending thermal fluids promotes boron-mineral dissolution, increasing boron concentration in thermal waters that discharge from the springs.

This scenario is confirmed by the $\delta^{11}B$ values of thermal waters samples that are anomalously low with respect to their principal circulation in the Mesozoic units (Figure 9). Indeed, if the thermal waters of meteoric origin (as the water isotopes suggest) circulated only in evaporate minerals units of marine origin, the value of $\delta^{11}B$ would range from 18‰ to 32‰ (Barth, 1993). The values of $\delta^{11}B$ of several of the thermal waters are even lower than the -5‰ characteristic of the Cimino volcanic rocks (Tonarini et al., 2003) or attributed to the flysch rock (Pennisi et al., 2000) but are rather comparable to those of hydrothermal tourmalines (Palmer, 1991) and local

tourmalines from Central Italy (Figure 9). Coupling the major ion content and $\delta^{11}B$ values, it is possible to show that thermal waters during their rising circulate within the flysch Ligurids (Figure 2). Because of the low permeability of these flysch units, the flow is very slow, giving the hot waters time to react and dissolve the borosilicate minerals within the flysch. A slow and tortuous path through the flysch units, with attendant conductive cooling, can explain the large temperature range of the thermal springs despite their relatively uniform chemical composition. Despite the presence of boron-rich minerals such as tourmaline in the Cimino-Vico province, the low boron concentration of the fresh waters circulating in the volcanics indicates the poor reactivity of these minerals in dilute waters and the relatively short water-rock interaction. The fresh waters acquire a boron isotopic signature which is a combination between the negative $\delta^{11}B$ of the volcanic products and the positive $\delta^{11}B$ of the recharge water (the rain water value approaches 40‰ near the coast; Pennisi et al., 2000), Figure 9.

Thus, in low enthalpy geothermal systems both strontium and boron isotopes can be used as conservative tracers since their chemistry is controlled more by the dissolution of the associated rocks and less by temperature-dependent fractionation into alteration minerals. Sr traces the interaction with the parent rocks and can be used to evaluate the mixing.

6. Conclusions

Chemical and multi-isotope data of fresh and thermal waters, sampled in the medium-low enthalpy hydrothermal system located in the Cimino-Vico volcanic district, have been studied. Water chemistry is controlled by mixing between fresh groundwater flowing in shallow volcanic rocks and thermal waters ascending from deep, high permeability Mesozoic limestones. Based on major element chemistry and the $\delta^{18}O$, δD, $\delta^{11}B$ and $^{87}Sr/^{86}Sr$ signatures of waters we conclude the following:

- The chemical composition of thermal waters (ranging from 25.3°C and 62.2°C) reflect long-term circulation within the deep geothermal reservoir in the Mesozoic evaporate-carbonate

formations. The chemistry of fresh waters (<24.2°C) differs from the composition of thermal waters and reflects interaction with the Na-K-rich Cimino-Vico volcanics.

- SO_4/Cl, Na/Cl and B/Cl of thermal watersdiffer from other hydrothermal systems in Central Italy, probably implying a lack of hydraulic continuity across the region.
- Based on the the $\delta^{18}O$ and δD of spring water, we infer that the recharge area for both the fresh and thermal aquifers is the summit region of Mount Cimino.
- Both $^{87}Sr/^{86}Sr$ and $\delta^{11}B$ can be used as tracer of groundwater mixing and circulation since they behave as conservative tracers in low-enthalpy thermal systems.The boron isotope composition of fresh waters is similar to those of the volcanic rocks constituting the aquifer, whereas the $\delta^{11}B$ values of thermal waters reflect dissolution of borosilicate minerals during fluid ascent from the deep aquifer.
- The $\delta^{11}B$ signature shows that thermal waters rising to the surface circulate within the low permeability flysch units.
- The thermal water flow path dictated by our geochemistry data (slow upflow) results in low spring temperatures that partially mask the heat resource of the reservoir. Our data are consistent with a large energy potential in this system.

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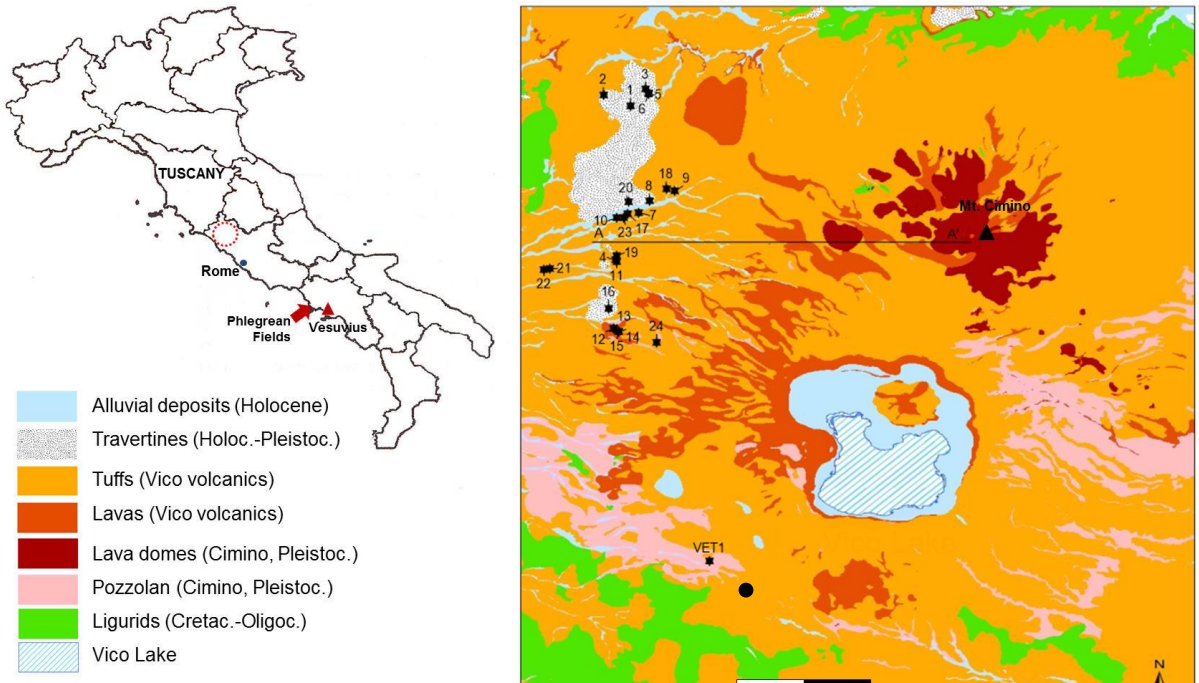
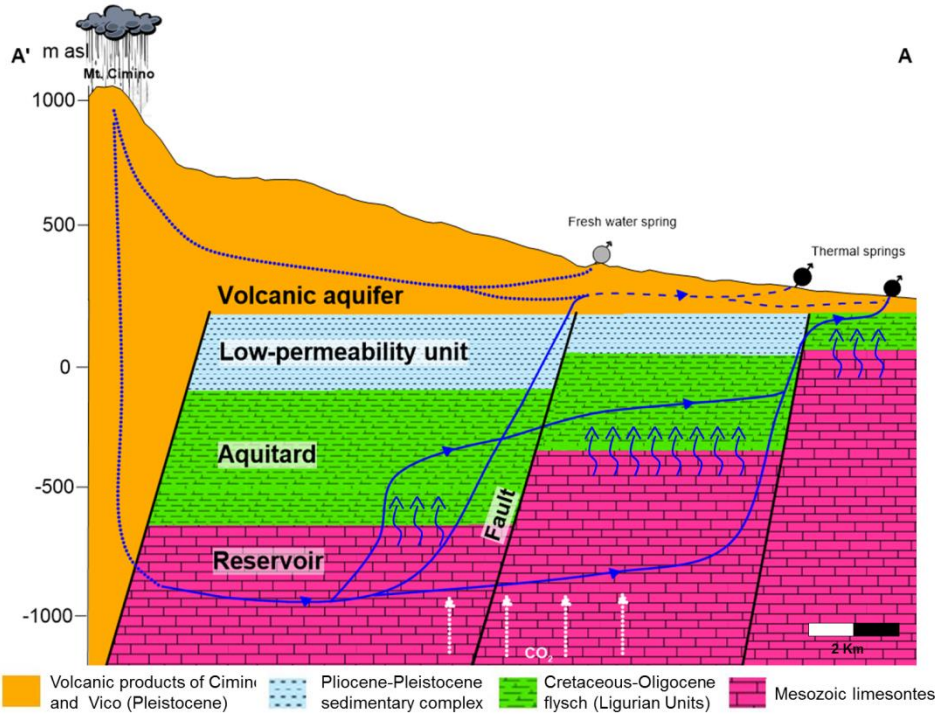


492

493 Figure 1. Study area. The dotted circle in the map on the top left represents the enlarged area from
494 where samples for this study were collected. The stares represent the sampling points and A-A' is
495 the location of the hydrogeological section in figure 2.The circle represents the geothermal well
496 VET1, see text for references.



497

498 Figure 2. Sketch of the hydrogeological setting of Cimino-Vico hydrothermal system and the
499 groundwater circulation along the A-A' section showed in Figure 1. Dotted lines represent fresh
500 water, solid lines thermal waters and dashed lines the mixing waters.

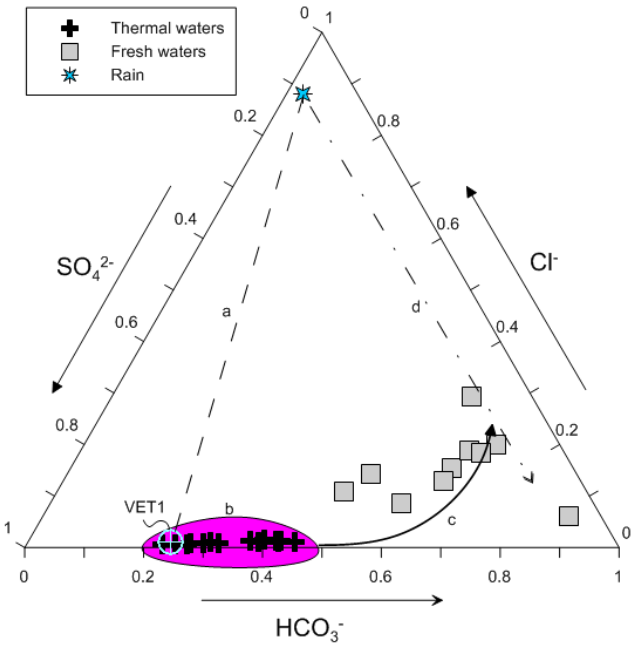


Figure 3. Anion composition of water samples (Equivalent/L) of fresh and thermal water: Dashed line (a) represents the enrichment in SO_4^{2-} content of rainwater that penetrates down into the geothermal reservoir. Grey area (b) is the interaction with carbonate minerals in the reservoir. Solid line (c) represents the mixing between thermal and fresh waters. Dashed dotted line (d) is the direct recharge of rain water to the shallow aquifer. VET 1 is the composition of the geothermal well Vetralla 001 (Figure 1).

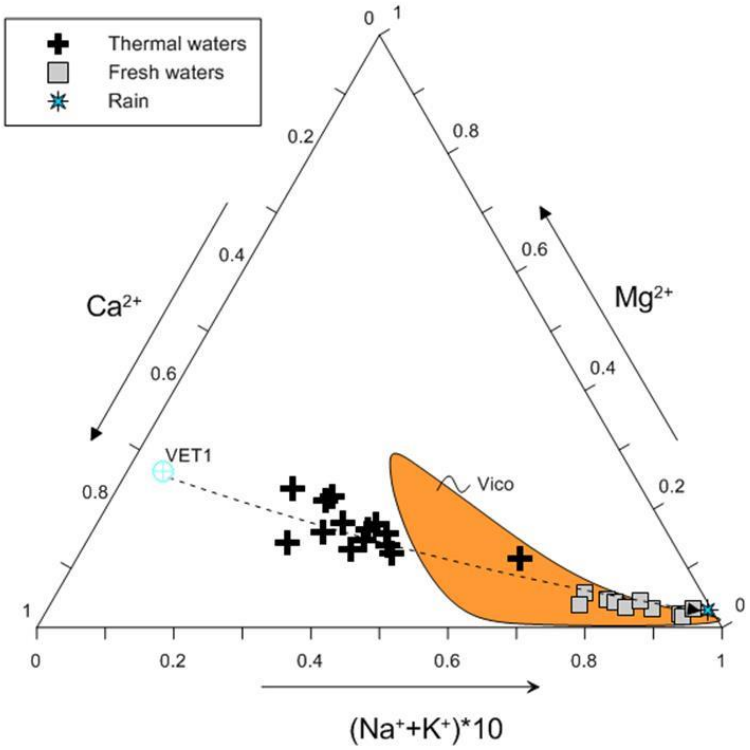
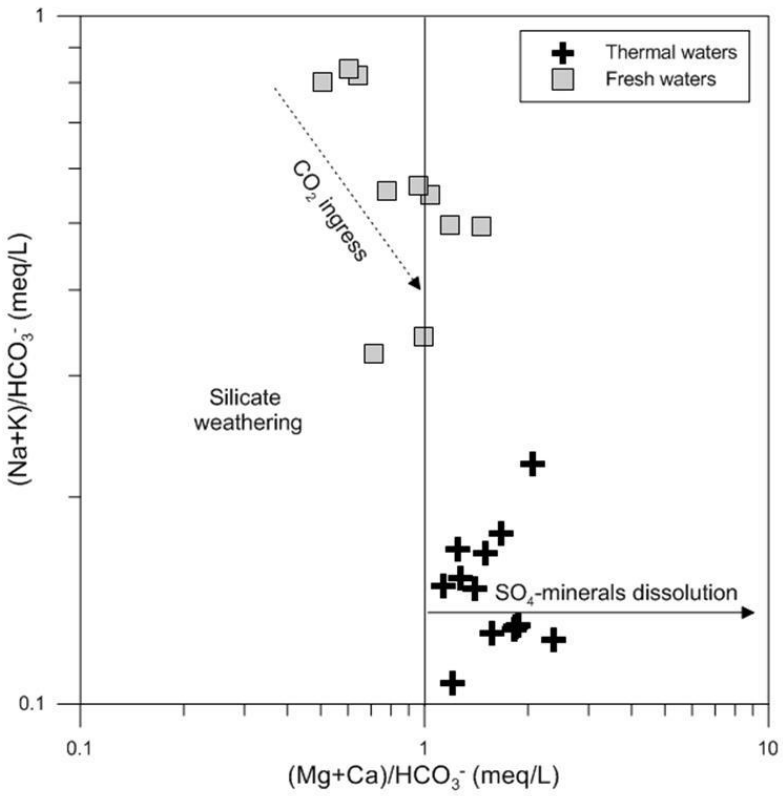
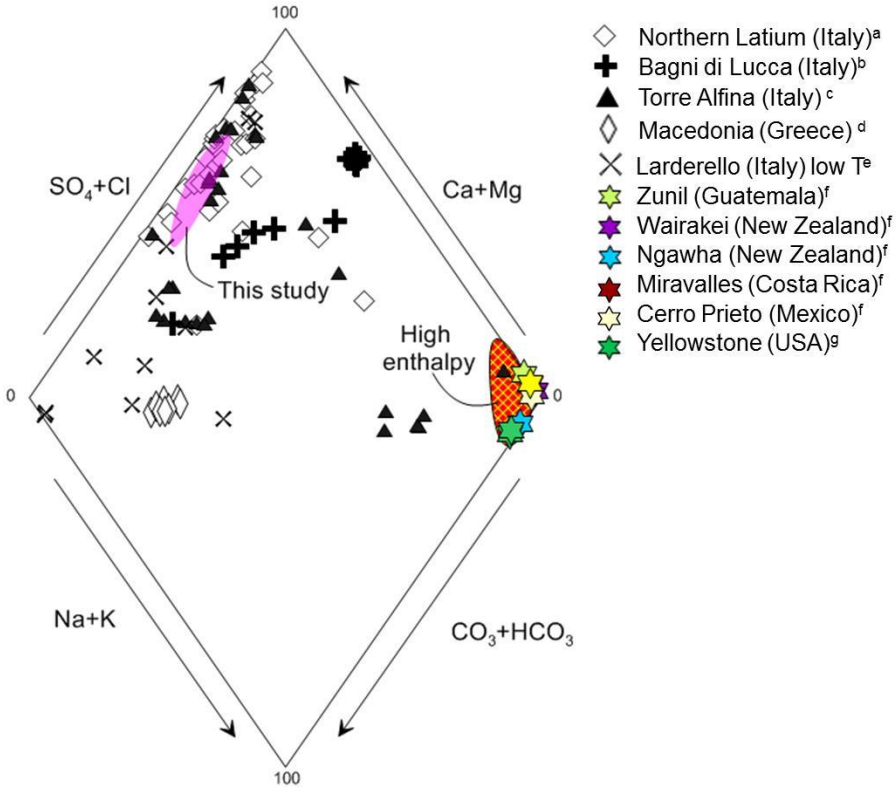


Figure 4. Cation composition of water samples (Equivalent) of fresh and thermal water: VET 1 is the composition of the geothermal well Vetralla 001 (Figure 1). Dashed line represents the mixing between thermal samples and rain water. Grey area shows the composition for the volcanic rocks related to the Vico volcanic activity (Gambardella et al., 2005).



513

514 Figure 5. Plot of $(Na+K)/HCO_3$ versus $(Ca+Mg)/HCO_3$. For details see text



515

516 Figure 6. Composition (Equivalent) of thermal waters from different geothermal systems. The
517 colored star symbols represent the water with T>100°C. a- Minissale et al., 2002; b- Boschetti et
518 al., 2005; c- Duchi et al., 1987; d- Dotsika et al., 2010; e- Duchi et al., 1986; f- Giggenbach 1988; g-
519 Thompson and DeMonge 1996.

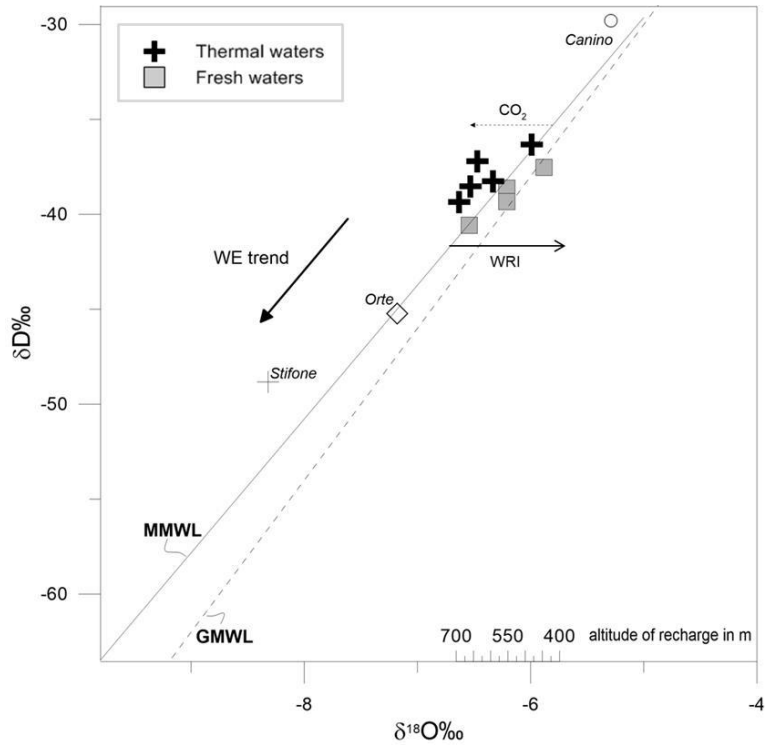


Figure 7. Water stable isotopes of the Cimino-Vico groundwater compared to the Global Meteoric Water Line (GMWL) (Craig, 1961), the Mediterranean Meteoric Water Line (MMWL) (Longinelli and Selmo, 2003) and other springs from Central Italy (Minissale, 2004). The black arrow indicates the geographical trend from West to East. WRI - Water-Rock Interaction.

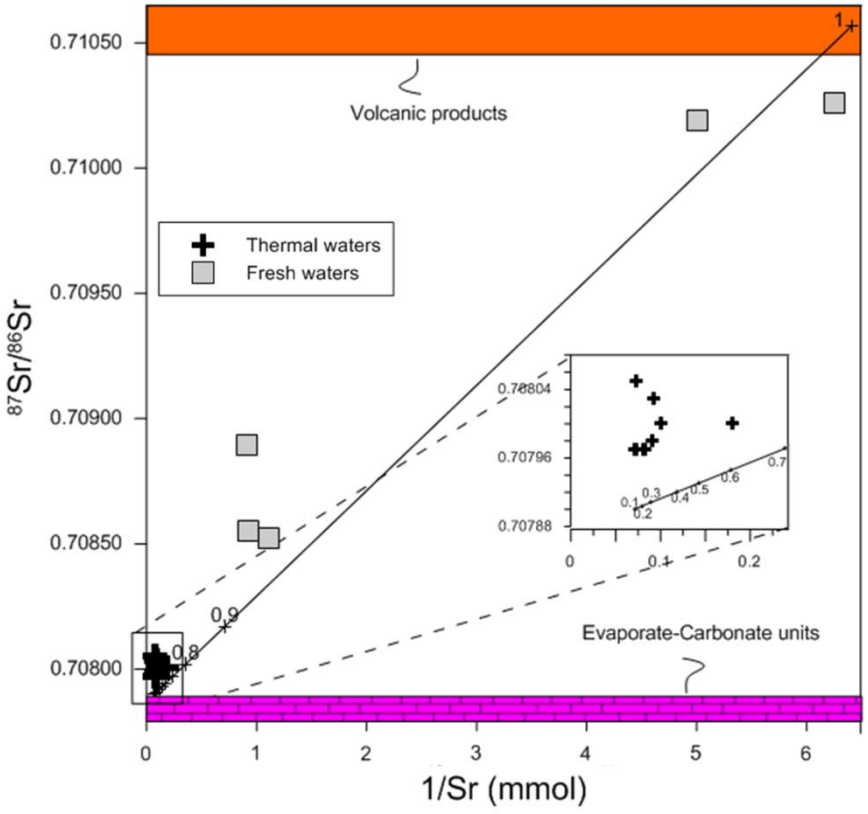


Figure 8. $^{87}Sr/^{86}Sr$ vs 1/Sr in the Cimino-Vico groundwater. The solid line is the calculated theoretical mixing line between the volcanic shallow aquifer end member and the evaporite-

carbonate units end member. The ratio of the Vico volcanic rocks is from Barbieri et al. (1979) and Hurley et al. (1966). The Sr concentrations of the evaporate-carbonate end member are from Cinti et al. (2014) and Minissale (2004).

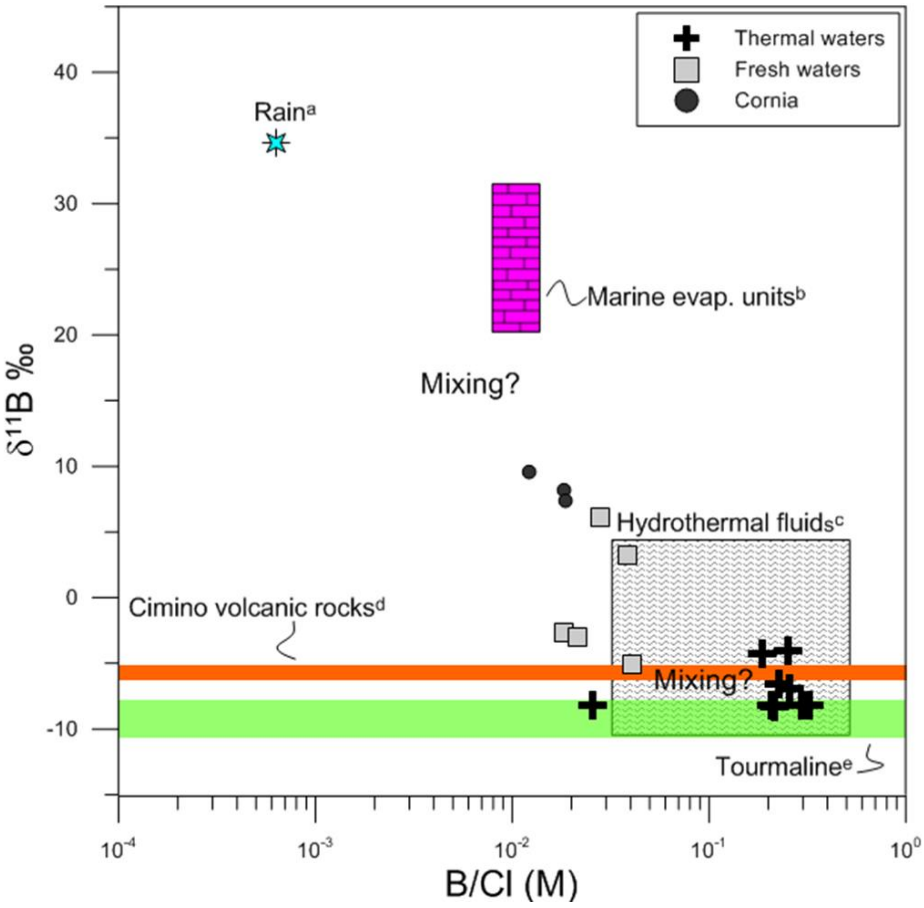


Figure 9. $\delta^{11}B$ vs B/Cl Molar ratio showing samples from this study and from: a- Rain water (Tonarini et al., 2009), b- Marine evaporite minerals (Barth, 1993), c- Hydrothermal fluids (Aggarwal et al., 2000; Aggarwal et al., 2003; Boschetti et al., 2013; Millot et al., 2012; Palmer et al., 1997), d-Cimino volcanics (Tonarini et al., 2003), e-Tourmaline (Leeman and Tonarini, 2001; Tonarini et al., 2003; Tonarini et al., 2009). References for thermal samples of Cornia (Pennisi et al., 2006).

539 Table 1. Physical parameters and chemical concentrations of groundwater in the Cimino-Vico district

Id	T°C	pH	EC	Ca	Mg	Na	K	HCO_3	Cl	SO_4	SiO_2	Sr	B	$\delta^{18}O$	δD	$^{87}Sr/^{86}Sr$	$\delta^{11}B$
			µS	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	‰	‰		‰
Fresh waters																	
2	17.3	7.4	719	58.2	17.0	49.3	15.9	275	76.5	35.9	-	-	-	-	-	-	-
9	20.0	7.0	603	64.6	12.8	27.2	23.5	160	35.6	117	75.4	0.90	0.15	-6.2	-38.6	0.70852	-2.62
13	24.2	6.4	446	67.0	13.8	24.7	17.0	186	24.1	123	63.5	1.10	0.26	-6.2	-39.3	0.70889	-3.00
14	19.4	7.8	305	9.32	6.71	15.9	25.5	122	20.4	14.8	61.2	0.20	0.22	-6.5	-40.6	0.71019	6.12
15	18.7	6.9	303	17.8	6.20	18.5	15.9	150	23.4	24.2	-	0.16	0.02	-	-	0.71026	3.25
15	19.5	7.2	476	25.3	5.80	33.7	37.4	177	29.6	33.6	-	-	-	-	-	-	-
18	18.1	6.8	753	107	13.8	36.0	25.6	397	45.8	112	78.1	1.08	0.26	-5.9	-37.5	0.70855	-5.00
22	18.7	7.1	771	82.1	13.7	37.1	45.0	308	26.1	133	-	-	-	-	-	-	-
23	19.9	6.7	749	85.3	17.3	28.2	52.8	488	19.2	23.4	-	-	-	-	-	-	-
24	20.3	7.6	342	18.5	5.10	15.9	29.9	128	17.9	32.0	-	-	-	-	-	-	-
Thermal waters																	
1	62.2	6.1	3170	558	146	33.8	31.5	1071	14.2	1968	49.4	12.3	1.12	-6.5	-37.2	0.70797	-6.99
3	60.0	6.3	2980	535	126	41.8	39.3	1129	14.5	1200	-	-	-	-	-	-	-
4	27.3	6.0	2460	473	120	34.2	32.9	638	9.01	1497	55.1	9.94	1.05	-6.0	-36.3	0.70800	-4.12
5	62.0	6.5	3010	585	143	34.5	32.1	1105	17.6	2268	49.7	11.0	1.12	-6.5	-38.5	0.70798	-4.25
6	57.0	6.5	2720	520	120	31.0	26.0	1145	14.5	1080	-	12.0	0.25	-	-	0.70797	-6.58
7	25.3	7.0	1720	243	73.5	33.4	71.1	619	12.4	727	-	5.61	1.08	-	-	0.70800	-8.24
8	54.7	6.5	2680	500	91.9	36.1	43.6	976	16.8	1051	-	-	-	-	-	-	-
10	41.1	6.3	3030	616	125	40.6	41.1	1037	14.2	1265	-	-	-	-	-	-	-
11	37.6	6.7	3400	608	141	41.8	39.6	976	12.8	1589	-	13.5	0.06	-	-	0.70805	-8.24
12	57.9	6.2	3190	681	149	32.5	31.1	1086	17.0	2845	48.3	13.7	1.15	-6.6	-39.3	0.70797	-8.37
16	59.6	6.1	3160	559	94.8	30.8	36.9	946	17.1	1228	-	-	-	-	-	-	-
17	31.1	5.8	2660	524	98.5	31.1	31.5	1040	19.0	1820	64.8	10.8	1.15	-6.3	-38.3	0.70803	-8.24
19	48.4	6.0	2700	474	95.9	36.6	37.4	1050	16.7	1099	-	-	-	-	-	-	-
20	51.4	6.1	3270	1003	155	32.8	46.0	1220	16.5	2579	-	14.0	1.56	-	-	0.70797	-8.24

540